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(54) Method for Preparing Heat-resistant Resin

(21) Application No.: Sho 53-[1978]-139,619

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Specification

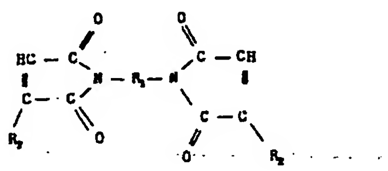
1. Title of the Invention

Method for Preparing Heat-resistant Resin

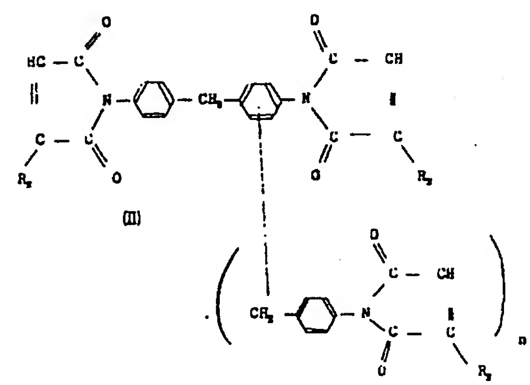
2. Scope of the Patent Claims

Method for preparing heat-resistant resin, characterized in that a resin composition comprising at least one of the maleimide compounds that can be represented by the general formulas (I) or (II) described below

general formulas



(I)



(II)

(in which R_1 denotes a divalent organic group containing at least 2 carbon atoms, R_2 denotes a hydrogen atom or an alkyl group and n denotes a number in the range of 0.5 to 5), an epoxy resin, a curing agent for the epoxy resin and a sensitizer is irradiated with light and the semi-cured product thus obtained is cured with heat.

3. Detailed Description of the Invention

The present invention pertains to a method for preparing heat-resistant resin. More specifically, the present invention pertains to a method for preparing heat-resistant resin, characterized in that a resin composition comprising maleimide compounds, an epoxy resin, a curing agent for the epoxy resin and a sensitizer is irradiated with light and the semi-cured product thus obtained is cured with heat.

Epoxy compounds are used in a wide variety of fields because they can become resins with excellent properties such as electrical properties, dimensional stability, reagent resistance, etc., when they are mixed with a curing agent having functional groups capable of reacting with an amino group and such an epoxy group as a carboxyl anhydride to allow reaction between the epoxy

group and the functional groups, forming a resin composition. However, these resin compositions are not necessarily useful from the standpoint of heat resistance.

A method involving the addition of a maleimide compound to an epoxy resin has been used to improve the heat resistance of the epoxy resin (Patent Publication No.: Sho 49-[1974]-12,600). The resin composition thus obtained indeed shows excellent heat resistance, but when it is exposed to an elevated temperature during the curing process, the viscosity of the resin will decrease, causing resin leakage prior to the curing and reducing the thickness of the resin or internally forming empty spaces, resulting in adverse effects especially on the electrical properties. For example, $\Delta\tan\delta$ may increase, the corona generation threshold may increase or the starting voltage of corona generation may decrease. Therefore, the resin composition may become unsuitable for use as an insulation composition. In view of the problems mentioned above, we carried out extensive studies in order to increase the heat resistance of the resin and to develop a process in which the resin leakage could be minimized during the process of impregnation or injection molding and were able to develop the present invention.

In the present invention, a resin composition comprising maleimide compounds, an epoxy resin, a curing agent for the epoxy resin and a sensitizer is irradiated with light and the semi-cured product thus obtained is cured with heat.

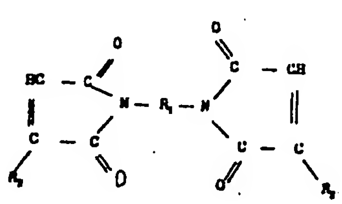
It has been shown that a maleimide compound can undergo photopolymerization. Moreover, it has also been shown that a polymer of maleimide compounds shows a very high heat-resisting property. For example, in the French Patent No. 1,455,514, a three-dimensional polyimide is formed by the heat polymerization of *N,N'*-disubstituted maleimide alone.

In the present invention, the maleimide compounds in the resin composition are irradiated with light at a low temperature in the presence of a sensitizer and undergo polymerization. The resulting three-dimensional crosslinks allow the formation of a network structure and a semi-cured state. The subsequent heat curing will result in curing of the epoxy resin and progress of the reaction of the maleimide compounds to induce complete curing and formation of a cured product with high heat resistance.

With the use of the method of the present invention, irradiation with light after impregnation will result in the formation of an impregnated state without resin leakage and injection molding without a mold will become possible.

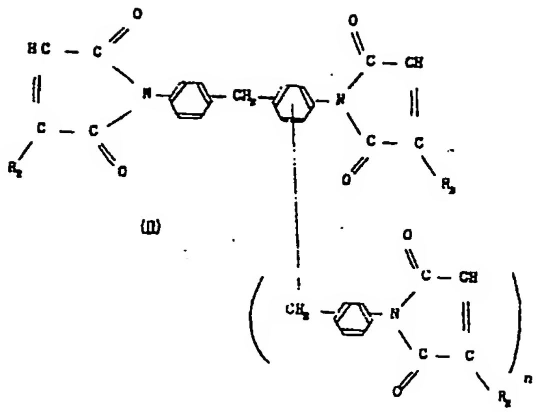
The maleimide compounds that can be represented by the general formulas (I) or (II) described below

general formulas



(I)

and



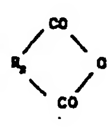
(II)

(in which R_1 denotes a divalent organic group containing at least 2 carbon atoms, R_2 denotes a hydrogen atom or an alkyl group and n denotes a number in the range of 0.5 to 5) can be used in the present invention.

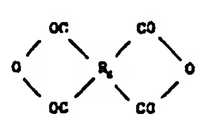
The maleimide compounds that can be represented by the general formula (I) include *N,N'*-(methylenedi-*p*-phenylene) dimaleimide, *N,N'*-(oxydi-*p*-phenylene) dimaleimide, *N,N'*-*m*-phenylene dimaleimide, *N,N'*-*p*-phenylene dimaleimide, *N,N'*-2,4-tolylene dimaleimide, *N,N'*-2,5-tolylene dimaleimide, *N,N'*-(sulfonedi-*p*-phenylene) dimaleimide, *N,N'*-(sulfonedi-*m*-phenylene) dimaleimide, *N,N'*-*m*-xylene dimaleimide, *N,N'*-*p*-xylene dimaleimide, *N,N'*-hexamethylene dimaleimide, etc. The maleimide compounds that can be represented by the general formula (II) include poly(phenyl methylene) polymaleimides.

The epoxy resins that can be used in the present invention include, for example, Epicoat 828, 834, 1001 and 1004 (Shell Co.) and GY–260 (Ciba Co.) of the bisphenol A diglycidyl ether type, DBN438 (Dow Co.) of the novolak type and Chissonox 221 and 289 (Chisso Co.) of the alicyclic type.

The curing agents that can be used in the present invention include acid anhydrides that can be represented by the general formulas given below.



or



(in which R_3 denotes an aliphatic, aromatic or alicyclic dicarboxylic acid residue and R_4 denotes an aliphatic, aromatic or alicyclic tetracarboxylic acid residue). Such acid anhydrides include, for example, phthalic anhydride, tetrahydrophthalic anhydride, methyl nadic [?] acid anhydride, methyl hexahydrophthalic anhydride, methyl tetrahydrophthalic anhydride, pyromellitic anhydride, benzophenone tetracarboxylic anhydride, butane tetracarboxylic anhydride, etc. They also include such metal salts as tricresyl borate, cobalt acetyl acetonate, zinc acetyl acetonate, zinc octylate, stannic octylate, triethanolamine titanate, etc.; metal chelate compounds, complexes of such Lewis acids as BF_3, PF_3 and an amine and such metal olefin compounds as ferrocene, etc. If necessary, they can be used in the form of a mixture.

In the present invention, it is desirable that 5-200 parts by weight of the maleimide compound are mixed with every 100 parts by weight of a mixture of the said epoxy resin and curing agent. When the amount of the maleimide used with respect to the amount of the mixture of the epoxy resin and curing agent used is less than 5 parts by weight, sufficient heat resistance cannot be obtained, while when the amount is greater than 200 parts by weight, heat resistance can be improved but the mechanical strength will be reduced.

The sensitizers that can be used in the present invention include polynuclear quinones (for example, anthraquinone, 1-chloroanthraquinone, etc.), benzoins, benzophenone, azobisisobutyronitrile, etc. The appropriate amount of the sensitizer used with respect to the amount of the maleimide used is in the range of 0.05-10 parts by weight. For monomers with a low degree of polymerization, the amount of the sensitizer used may be increased in order to promote the polymerization reaction.

The resin composition of the present invention is formed into an impregnated product or an injection-molded product and then irradiated with light with the use of a low pressure mercury vapor lamp, a high pressure mercury vapor lamp or an ultrahigh pressure mercury vapor lamp to obtain a semi-cured product. The semi-cured product thus obtained is cured by heating to complete the process.

The present invention will be explained concretely below with the use of actual examples.

Actual Example 1

Forty-seven parts by weight of [Epicoat 828], 15 parts by weight of poly(phenyl methylene) polymaleimide, 37 parts by weight of methyl tetrahydrophthalic anhydride, 0.2 part by weight of [DMP 30] and 0.5 part by weight of benzoin as the sensitizer were blended to obtain a resin composition. The resin composition thus obtained was irradiated with light under a 300 W photographic lamp. It was confirmed that a semi-cured product, the surface of which gave a dry touch to the finger, could be obtained after 20 minutes of irradiation. Subsequently, the temperature was raised to 150°C for 10 hours of curing and then to 200°C for 5 hours of curing to obtain a cured product. Almost no resin leakage could be detected during the aforementioned processes and distinctive light irradiation effects could be achieved.

A test bar formed by wrapping an uncoated steel bar measuring 400 mm x 3.2 mm x 6.5 mm with a Tetoron film and then with a glass cloth tape was impregnated with the resin composition using the impregnation curing process; no leakage of the resin could be detected during the process. The product gave very stable dielectric loss; $\tan\delta$ was 0.1% at 25°C, 1 kV and 3.0% at 200°C, 1 kV with $\Delta\tan\delta$ 1 kV-3 kV of 0.3%. The corona discharge rate was also low, 0.90

x 10^3 times/second at 10^{-10} Coulomb. The corona discharge starting voltage was high, 3.0 kV. Namely, the product showed excellent electric properties. Furthermore, the resin monomer showed excellent mechanical strength; the bending strength measured at 25°C was 14.5 kg/mm^2 and the bending strength after 500 hours at 240°C of aging was still 10.1 kg/mm^2, indicating that the product showed excellent heat stability and mechanical properties.

Actual Example 2

Ten parts by weight of [Epicoat 828], 10 parts by weight of [DEN 438], 5 parts by weight of [Chissonox 221], 20 parts by weight of hexahydrophthalic anhydride, 10 parts by weight of *N,N'*-(methylenedi-*p*-phenylene) dimaleimide, 40 parts by weight of poly(phenyl methylene) polymaleimide and 0.5 part by weight of benzoin ethyl ether as the sensitizer were blended to obtain a resin composition. The resin composition thus obtained was impregnated into a glass cloth and irradiated with a 100 W high pressure mercury vapor lamp for 30 min. Subsequently, the product was cured at 150°C for 10 hours and then at 180°C for 10 hours to obtain a cured product. Almost no leakage of resin could be detected during the said processes and the light irradiation effects could be achieved. The cured resin product thus obtained gave a bending strength at 25°C of 14.0 kg/mm^2. Its bending strength measured after it had been subjected to aging at 240°C in air for 500 hours was 10.5 kg/mm^2.

The results of the test bar test performed as described in Actual Example 1 were as follows: tanδ was 0.20% at 25°C, 1 kV and 3.0% at 200°C with Δtanδ 2 kV-3 kV of 0.30%. Its corona characteristics were excellent, almost identical to those observed in Actual Example 1.

Actual Example 3

Sixty parts by weight of [Epicoat 828], 40 parts by weight of methyl tetrahydrophthalic anhydride, 1 part by weight of tris(dimethyl aminomethyl) phenol, 5 parts by weight of *N,N'*-(oxydi-*p*-phenylene) dimaleimide and 0.8 part by weight of 1-chloroacetoquinone as the sensitizer were blended to obtain a resin composition. The resin composition thus obtained was cured according to the procedure used in Actual Example 2. There was no leakage of resin during the procedure.

The characteristics of the cured resin thus obtained were as follows: a bending strength at 25°C of 14.5 kg/mm^2 and a bending strength of 9.2 kg/mm^2 measured after it had been subjected to aging at 240°C in air for 5 hours. The results of the test bar test performed as described in Actual Example 1 were as follows: tanδ was 0.1% at 25°C 1 kV and 4.5% at 200°C with Δtanδ 1 kV-3 kV of 0.50%. Its corona characteristics were excellent, almost identical to those observed in Actual Example 1.

Actual Example 4

Sixty-five parts by weight of [Epicoat 828], 35 parts by weight of poly(phenyl methylene) polymaleimide, 0.5 part by weight of tricresyl borate, 0.5 part by weight of triethanolamine titanate and 1.0 part by weight of anthraquinone as the sensitizer were blended to obtain a resin composition. The resin composition thus obtained was cured according to the procedure used in Actual Example 1. There was no leakage of resin during the procedure.

The characteristics of the cured resin thus obtained gave a bending strength at 25°C of 15.0 kg/mm^2 and a bending strength of 9.2 kg/mm^2 measured after it had been subjected to aging at 240°C in air for 5 hours.

The results of the test bar test performed as described in Actual Example 1 were as follows: $\tan\delta$ was 0.25% at 25°C, 1 kV and 4.5% at 200°C with $\Delta\tan\delta$ 1 kV-3 kV of 0.60%. Its corona characteristics were excellent, almost identical to those observed in Actual Example 1.

The products obtained from Actual Example 1-Actual Example 4 all showed excellent heat stability, mechanical properties and electric characteristics.

Comparison Examples are given below.

Comparison Example 1

In comparison with the resin composition obtained from Actual Example 1, a resin composition was prepared by blending 47 parts by weight of [Epicoat 828], 15 parts by weight of polyphenyl methylene polymaleimide, 37 parts by weight of methyl tetrahydrophthalic anhydride and 0.2 part by weight of [DMP 30] as described in Actual Example 1. The resin composition thus obtained was impregnated on the test bar identical to that used in Actual Example 1 and cured by heating at 150°C for 10 hours and then at 200°C for 5 hours. The amount of resin leakage per test bar was 10 g and $\tan\delta$ was 0.15% at 25°C, 1 kV and 3.0% at 200°C 1 kV but with $\Delta\tan\delta$ 1 kV-3 kV of 5.0%, a very high value. The number of corona discharges at 10^{-10} Coulomb was 2.50×10^8 times/second and the corona discharge starting voltage was 1.38 kV. Compared with Actual Example 1, the resin composition obtained in this comparison example showed a marked decrease in electric characteristics due to varnish leakage.

Agent: N. Katsuno, Patent Attorney (and one other)

Procedural Revision (Voluntary)

Date: March 23, 1979

To: Mr. Patent Officer

1. Expression of the Event: Patent Application No. Sho 53-[1978]-139,619

2. Title of the Invention: Method for Preparing Heat-resistant Resin

3. Party Requesting the Revision:

Relationship to the event: Patent Applicant
Address: 2-3, 2-chome, Marunouchi, Chiyoda-ku, Tokyo-to
Title (601): Mitsubishi Electric Co. Ltd.
Representative: T. Shinto

4. Agent:

Address: Mitsubishi Electric Co. Ltd.
2-3, 2-chome, Marunouchi, Chiyoda-ku, Tokyo-to
Name (6699): N. Katsuno, Patent Attorney
(Communication: 03(435)6095 Patent Division)

5. Object of Revision: "Detailed Description of the Invention" section of the Specification

6. Contents of Revision: Specification is revised as described below

Page	line	before revision	after revision
8	17	/-chloro	1-chloro
12	1	/-chloro	1-chloro

That is all.